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A PCB SURVEY OF WINTER SNOWPACK IN PRINCE EDWARD ISLAND: 1981-82

IWD-AR-WQB-84-54

INLAND WATERS DIRECTORATE
ATLANTIC REGION
WATER QUALITY BRANCH
MONCTON, NEW BRUNSWICK

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ENVIRONMENT CANADA

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A copy will be made available in French upon request

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ABSTRACT

During the first week of March in 1981, a snowpack sampling survey was carried out in Prince Edward Island. The samples were subsequently analysed for polychlorinated biphenyls (PCB's) and organochlorine pesticides. Observed PCB concentrations ranging between 2.3 ng/L and 9.0 ng/L were significantly lower than those reported in snow from the Great Lakes Region. Analysis of wet precipitation (rain and snow) taken at Ellerslie-P.E.I. during the corresponding period indicated relatively high levels of PCB's which implies that a local source(s) is most likely responsible for contamination of samples at this site. The only other compounds found in the samples were α-BHC and γ-BHC (Lindane) at concentrations much lower than those usually found in rain.

SOMMAIRE

Pendant la première semaine de mars 1981, des échantillons de neige furent prélevés dans l"Ile du Prince-Edward. Les échantillons de neige fondue furent par la suite analysés pour la présence de biphényles polychlorés (BPC) et de pesticides organochlorés. Des concentrations de BPC variant entre 2,3 ng/L et 9,0 ng/L furent observées dans la neige. Ces concentrations représentent des niveaux inférieurs et insignifiants quand elles sont comparées aux résultats rapportés auparavant pour de la neige prélevée dans la région des Grands Lacs. Toutefois les données tirées d'analyses d'échantillons de précipitations humides provenant de Ellerslie-I.P.E. pour la période coïncidente démontrent des niveaux relativement élevés, suggérant qu'une source(s) locale de contamination fut responsable. Les seuls autres composés trouvés furent le α-BHC et γ-BHC (Lindane) et ce a des teneurs beaucoup inférieures à celles normallement mesurées dans la pluie.

INTRODUCTION

The presence of trace organic contaminants in atmospheric precipitation is certainly not a new occurrence. Organochlorinated pesticides (OC's) and polychlorinated biphenyls (PCB's) were observed eight years ago by Strachan et al.(1) in snow and rain samples collected during winter on the Canadian side of the great lakes. Similar results by other workers corroborated these findings which raised much concern on the importance and impact of long range transport of airborne pollutants on the Canadian environment.

Consequently in 1977 the Inland Waters Directorate established the "Canadian Network for Sampling Organics in Precipitation", commonly known as "CANSOC". The intent of this precipitation sampling network was to study and evaluate the occurrence of OC's and PCB's in precipitation collected at sites located in all regions of the country. Findings reported by Brooksbank (2) confirmed the ubiquitous nature of such compounds as PCB's, BHC's and traces of other chlorinated pesticides in this media.

In September 1980, Water Quality Branch - Atlantic Region installed two wet precipitation collectors in the region, one in Kejimkujik National Park, N.S. and the other at the Ellerslie Fisheries Research Station in Prince Edward Island. In addition to monitoring PCB's and OC's, WQB also looked for the presence of polyaromatic hydrocarbons (PAH's) and chlorinated benzenes (CB's). The principal findings of these studies by the author (3) confirmed the presence of PCB's and

BHC's. In addition fluoranthene, a non-carcinogenic PAH was observed in the majority of samples. However, relatively high concentrations of PCB's were noted in samples from the P.E.I. Fisheries Station compared to samples from other sites in the region. An average PCB concentration of 0.14 ug/L was calculated for the one year period between September 1980 and September 1981. Anomolous high values ranging between non-detectable concentrations up to 0.43 ug/L raised concern over the matter and prompted a further investigation (4) which confirmed PCB fallout in soil samples from the area. Because nearby point sources were unknown at the time, the assumption was made that the problem could be affecting most of P.E.I.

In light of available information, it was recommended that a more extensive study be undertaken to establish the extent of PCB fallout on the Island. In view of this it was decided that an Island-wide survey of snowpack would be more amenable. The study goals were aimed mainly at identifying any abnormal amount and pattern of PCB fallout and if possible a general indication of the responsible point source(s). The report presents results obtained from the survey and attempts to interpret their environmental significance.

EXPERIMENTAL

Sampling Locations

Eleven sites in P.E.I. were sampled for snowpack during the period between March 1 and March 4, 1982. With the exception of site No. 11 (Figure 1), all sites were situated on the perimeter of the province.

In addition, six sites were sampled in Eastern New Brunswick and

Northern Nova Scotia. The map in Figure 1 shows their geographic distribution. The mainland sites were sampled both before (site No. 13) and after (sites Nos. 12, 14-16) the survey in P.E.I. Table 1 provides a detailed description of the sampling locations.

There were abundant amounts of snow over most of P.E.I. during the winter of 1982 with the exception of the south eastern section in the vicinity of Little Sands. The ground there was covered with slight amounts of snow over a thin sheet of ice.

Each site location was scouted to determine the best place for collecting the sample. A snowmobile and sled were used in places where sites were too far and snow too deep for walking. In other areas snowshoes and a small sled were used to access sites close to the mobile laboratory. Special consideration was taken in choosing sites that were remote from main roads and habitation, thus avoiding power lines, transformers, capacitors and any other potential source of contamination. In most places, sites were chosen in enclosed areas such as wood clearings which should be more representative of the season's snowfall and not been subjected to serious disturbances, such as drifting snow, fallen debris or snowmobile activity.

SAMPLING METHOD

The Water Quality Branch mobile laboratory proved very valuable in the field for the preparation of samples in a contamination-free environment.

Galvanized buckets with 63 L and 12 L holding capacities were used to collect and thaw the snow samples, respectively. A small aluminum

shovel was used for sampling the cores and mixing the sample. Four litre amber glass bottles with teflon lined caps were used to store the melted samples. Pesticide grade hexane and acetone, for rinsing of apparatus, were stored in their original containers equipped with all-glass dispensers. All utensils were scrupulously cleaned, first with soap and water, followed by rinsing with ample amounts of acetone, chloroform, hexane:acetone (1:1) and final rinse with hexane. The final hexane washings were analyzed to ascertain contamination-free apparatus.

At the site a trench measuring approximately 75 cm x 150 cm was dug almost to ground level. Using the small aluminum shovel, 10 cm of snow was carved off a trench wall and discarded, snow cores measuring approximately 20 cm x 10 cm were then cut and transferred to the large galvanized bucket. A 35 L to 40 L sample was collected and thoroughly mixed. A lid was then immediately placed on the bucket and transported to the mobile laboratory.

In the mobile laboratory, the snow was gradually melted in two 12 L galvanized buckets over propane burners, the water temperature never exceeding 2-3^{o}C. The snowmelt was then poured into two 4 L bottles and labelled appropriately. All sampling apparatus and utensils were then rinsed with acetone and hexane and wrapped in aluminum foil.

ANALYTICAL METHOD

Samples were analyzed as soon as they arrived to the main laboratory in Moncton, usually not more than four or five days after collection. Prior to extraction, the samples were filtered through a 60-80 mesh brass sieve (250 u) to remove foreign materials such as soft wood needles, small pieces of bark, and grit. The extraction procedure followed was essentially that proposed by "Le comite de normalisation des méthodes d'analyse du ministère de l'environnement du Québec" (5). The method consisted in extracting approximately 1.5 L aliquots of the 8 L sample with hexane in a separatory funnel. After all of the 8 L sample was extracted the hexane extracts were pooled, dried by passing through a column packed with sodium sulphate and concentrated on a rotary evaporator to a volume of 10-15 mL. In a centrifuge tube the extract was further concentrated to a final volume of 1 mL under a gentle stream of nitrogen.

The procedure of Murphy (6) was employed to eliminate high background interferences by treating the hexane extracts with concentrated sulfuric acid. Fluorisil column fractionation (7) was used to further improve chromatographic analysis.

Instrumental analysis was performed using a Varian-3700 capillary gas chromatograph. The splitless injector and electron capture detector were maintained at 270°C and 340°C respectively. The 50 m x 0.5 mm I.D. glass SCOT column (OV-17) was programmed from 70°C (2 min.) at 7°C/min to 220°C for a final hold of 50 min. A Spectra Physics 4000 data system was used to integrate chromatograms and perform post run calculations.

The electron capture quantitation methodology employed was that of Webb & McCall (8) later modified by Chau and Sampson (9). By this method isomeric PCB contributions were reported as total arochlors. Because of the low concentrations in the samples, quantitation using a 100 pg/uL mixture of arochlors 1242:1254:1260 (1:1:1) was used instead of the commonly used 600 pg/uL.

Confirmation of peak identity was achieved by analysing the sample extract on a G.C. column of different polarity. For this purpose a Tracor MT-222 G.C. equipped with a pulse mode electron capture detector was used. A column, 1.8 m x 4 mm I.D., coated with 3% OV-101 was used under isothermal conditions at 190°C. The injector and detector were maintained at 220°C and 325°C respectively.

Water samples fortified with PCB's and control/reagent blanks were prepared and analysed concurrently with field samples to confirm the reliability of the methods and to ensure that samples were not contaminated in the field or in the laboratories.

DISCUSSION

PCB's and OC pesticides along with their respective limits of detection are listed in Table 2. It should be noted that the acquisition of larger snowmelt sample volumes of eight litres rather than one litre contributed approximately to a ten-fold increase in sensitivity, albeit necessary to detect the very low concentrations that were sought and reported in Table 3. The other pesticides listed in Table 2 were not identified in any of the samples at the limits of detection specified.

Samples spiked with PCB's, distilled water blanks and reagent blanks were analysed concurrently with the snowmelt samples. The PCB spikes yielded greater than 85% recovery and the reagent blanks produced very clean extracts. However, Millipore purified tap water contained 3.3 ng/L PCB (n = 4, S.D. = 0.43), 0.18 ng/L α-BHC (n = 4, S.D. = 0.05) and 0.12 ng/L γ-BHC (n = 4, S.D. = 0.09). The presence of these components in the Millipore water did not interfere in the analysis of samples as verified by analysing reagent and glassware blanks.

In Prince Edward Island samples, the PCB concentrations ranged between 2.3 ng/L and 9.0 ng/L with a mean value of 4.6 ng/L (Table 3). In New Brunswick and Nova Scotia, mean PCB concentrations of 4.0 ng/L and 1.9 ng/L were observed, respectively. These results represent very low concentrations relative to what had previously been reported in the literature. For example, Swain (11) reported PCB values ranging between 50 ng/L and 230 ng/L in snow collected during 1976 from various sites near Lake Superior. Strachan (1) on the other hand found PCB concentrations varying between 18 ng/L and 43 ng/L in snow samples taken from sites on the Canadian side of the Great Lakes during the winter of 1975-76. In the first study hexane, methylene chloride and chloroform were used for extraction whereas XAD-2 resin column extraction with ether and benzene elution were used in the latter work. The inclusion of polar solvents in the first method may explain the higher concentrations obtained due to the greater extraction efficiency of such solvents in regards to adsorbed PCB's on particulates.

In the present study, hexane was used for extraction which

tentatively leads to the assumption that recoveries could be low, due to poor efficiency in extracting PCB's from particulates present in the snow samples.

However, if this explanation is valid, it does not corroborate the data in Table 4 which correspond to samples collected on a monthly event basis during the same period. Mean PCB concentrations of 210 ng/L and 69 ng/L were observed in the Ellerslie-P.E.I. and Kejimkujik Park samples respectively. The extraction procedures being the same would indicate in an analogous way the quantitative recovery of PCB's from the snow samples. In light of this, the relatively low values in snowpack seem to show a loss of PCB's during the course of the winter probably through the volatilization process whereas sub-event samples in Table 4 which are collected at least once a week and preserved were not comparitively subjected to the same conditions and elements.

Examination of the α-BHC and γ-BHC isomer data in Table 3 and 4 leads to the same conclusion. Respectively, α-BHC and γ-BHC (Lindane) are approximately 1.2 and 1.4 orders of magnitude lower in snowpack relative to the corresponding integrated monthly event samples. Compared to rain, Strachan (1) reported very similar reduced levels of OC's in snowmelt with the exception of PCB's which remained high. It is noteworthy to mention that the BHC data compared very well with that of the previous author for both the snowpack and rainwater data, considering that the studies were carried out six years apart. This information confirms once again the widespread and persistent nature of these compounds and to some extent how they move throughout the environment. DDT and methoxychlor were not detected in our samples.

In general, it can be said that PCB concentrations were relatively low in the P.E.I. snowpack samples (background levels) compared to corresponding wet precipitation (event) samples. Concentrations were also significantly lower than those reported on integrated snow samples from the Great Lakes Region. Overall there were just three PCB levels above the group median. These low levels were located in P.E.I. at site 4 (9.0 ng/L), site 5 (5.9 ng/L) and site 9 (8.4 ng/L). Trends, fallout patterns or point sources were not discernible from the data. Finally, it can be concluded that the unusually high concentrations of PCB's reported previously (3,4,10) were probably mostly due to local contamination from unknown sources.

ACKNOWLEDGEMENTS

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FIGURE 1. ILLUSTRATION OF SAMPLING STATIONS

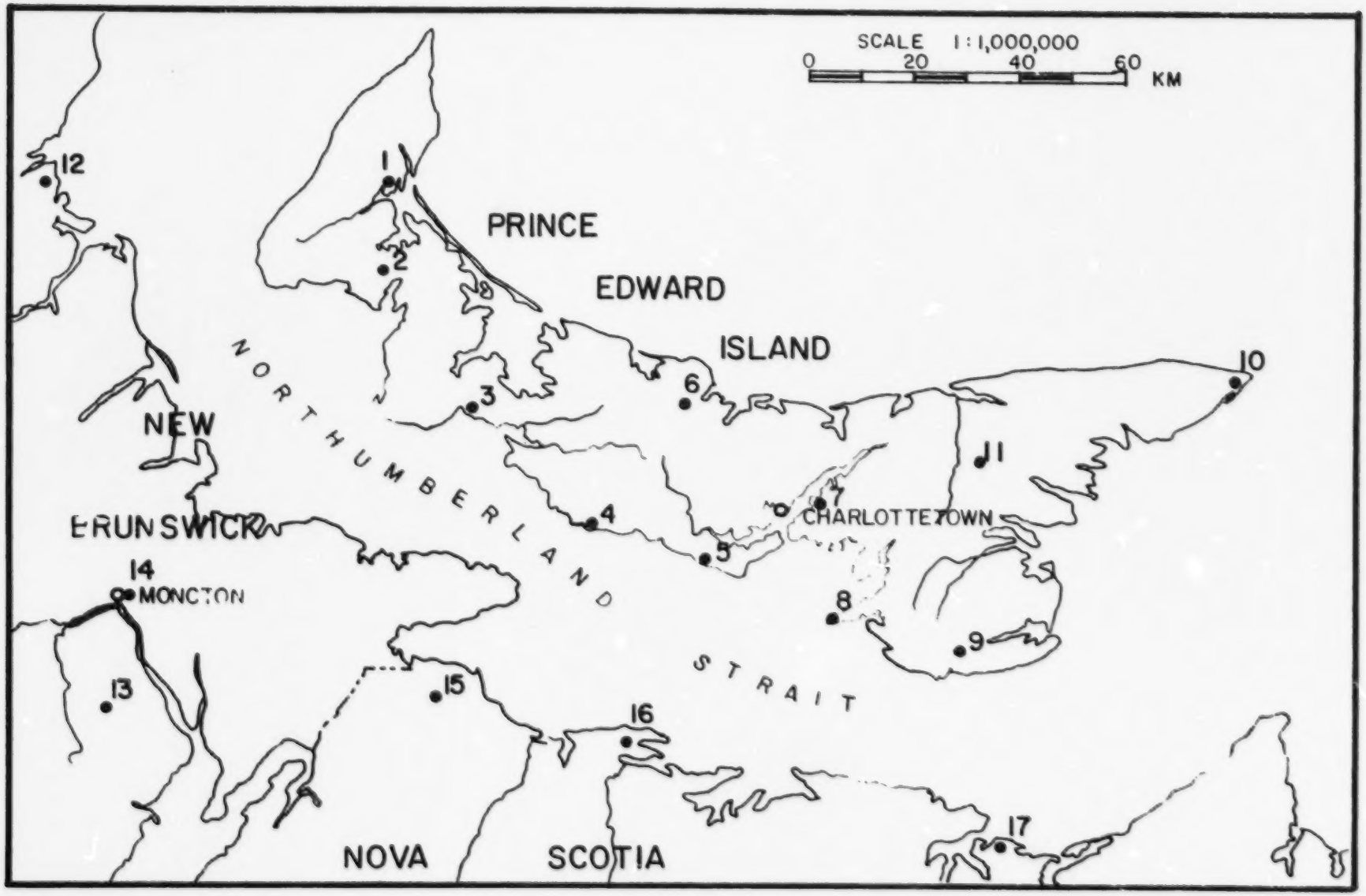

TABLE 1. LIST OF SAMPLING STATIONS

St.#	Station Name	Description of Sampling Station	U.T.M.*	Date of Sampling
		Prince Edward Island		
1	Hwy 171	Approx. 1.3 km from intersection of Hwy 2 at Bloomfield Corner (300 m N of Hwy 171)	E4111 N51787	04/03/82
2	Hwy 138	2.0 km N of bridge at Alaska (300 m E of Hwy 138)	E4152 N51650	04/03/82
3	Hwy 11	2.5 km E of intersection at St. Nicholas (50 m N of Hwy 11)	E43005 N514105	04/03/82
4	Augustine Cove	Near road to Camp Abegweit 1.2 km S of Hwy 10 (200 m E of Camp road)	E4545 N511775	01/03/82
5	Argyle Shore	0.85 km W of Amentry and 0.65 km N of Hwy 19	E47045 N51142	01/03/82
6	Hwy 224	0.6 km S of intersection of Hwy 229, near New Glasgow (300 m N of Hwy 224)	E4709 N51399	03/03/82
7	Mermaid	At upper road to Munn's Point, 200 m from Hwy 21	E4963 N512205	03/03/82
8	Point Prim	At Hwy 209 extension, near lighthouse (75 m N of Hwy)	E4970 N50999	03/03/82
9	Little Sands	At unnamed Hwy to Hwy 201, 1.3 km N of Hwy 4 (100 m W of road)	E5279 N50914	02/03/82
10	East Point	1.3 km from Hwy 16 on road to lighthouse (50 m N of road)	E5781 N51445	02/03/82
11	Hwy 313	2.5 km S of intersection of Hwy 331 and 75 m E of Hwy 313 (7.5 km S of St. Peters)	E5304 N51305	03/03/82

		New Brunswick			
12	Kouchibouguac	National Park at Callanders Beach road, 100 m from main road	E3536	N518515	12/03/82
13	Hwy 910	4.3 km E of Turtle Creek intersection (50 m N of Hwy 910)	E3576	N50899	25/02/82
14	Moncton	Between Humphrey and Leslie St. (tennis court)	E3609	N51067	12/03/82
		Nova Scotia			
15	Tidnish Crossroad	Unnumbered Hwy to Tidnish Crossroads, about 4.8 km N of Head of Amherst (50 m W of road)	E4245	N508685	10/03/82
16	Wallace Bay	Secondary road from Wallace Bay to Fox Harbour, 3.5 km E of Wallace Bay (50 m N of road)	E4591	N507625	10/03/82
17	Hwy 348	1.5 km E of Crossroads to Marshalls Crossing (100 m S of Hwy on new side road)	E5307	N505725	09/03/82

* Universal Transverse Mercator Grid

TABLE 2. LIST OF PCB'S AND OC'S DETERMINED IN THE SNOWMELT SAMPLES

PARAMETER	DETECTION LIMIT (ng/L)*
Total Arochlors (1242:1254:1260)	2.
α-BHC	0.1
Lindane (γ-BHC)	0.1
Heptachlor	0.1
Aldrin	0.1
Heptachlor Epoxide	0.1
α-Chlordane	0.5
γ-chlordane	0.5
p,p'-DDE	0.2
o,p'-DDT	0.2
p,p'-DDD	0.2
p,p'-DDT	0.2
Mirex	0.5

* Based on 8.0 L Sample

TABLE 3 CONCENTRATION OF PCB'S AND BHC'S IN SNOWMELT SAMPLES

Station #	Sample Volume (L)	Final Concentration in Snow (ng/L) PCB-total	α-BHC	γ-BHC
Prince Edward Island				
1	8.0	3.8	1.2	0.21
2	7.8	2.7	1.2	0.23
3	8.0	2.6	1.8	0.28
4	8.0	9.0	0.61	0.15
5	8.0	5.9	0.97	0.13
6	8.0	4.2	1.7	0.52
7	7.8	4.3	1.2	0.62
8	8.1	3.1	0.66	0.32
9	8.1	8.4	0.68	0.25
10	8.1	2.3	1.5	0.25
11	7.5	4.9	0.71	0.24
		$\bar{x}$ = 4.6	1.1	0.29
New Brunswick				
12	8.1	3.3	1.5	0.19
13	8.1	4.6	1.0	0.19
14	8.0	4.0	1.2	0.18
		$\bar{x}$ = 4.0	1.2	0.19
Nova Scotia				
15	8.1	1.8	1.5	0.24
16	8.0	2.2	0.87	0.18
17	8.1	1.8	1.2	0.17
		$\bar{x}$ = 1.9	1.2	0.20
		$\bar{x}$ = 4.1	1.2	0.26

TABLE 4: WET PRECIPITATION EVENT DATA* COLLECTED WITH THE SANGAMO SAMPLER DURING THE WINTER OF 1981-82 AT ELLERSLIE, P.E.I. AND KEJIMKUJIK NATIONAL PARK IN N.S.

Monthly Event	Volume (L)	Total PCB's	α-BHC	γ-BHC
		(ng/L)		
Ellerslie, P.E.I.				
Dec/81	5.0	120	45.	23.
Jan/82	3.2	220	8.0	4.0
Feb/82	1.7	400	12.	4.0
Mar/82	1.7	100	10.	2.0
		$\bar{x}$ = 210	19.	8.2
Kejimkujik, N.S.				
Dec/81	6.2	100	30.	16.
Jan/82	6.9	45	9.0	0.6
Feb/82	4.2	38	10.	1.0
Mar/82	4.4	91	22.	3.0
		$\bar{x}$ = 69	18.	5.1

* Ref. No. 3, 10